

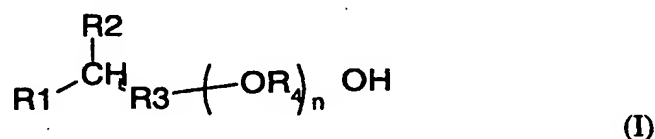
LOW FOAMING FORMULATION OF GLYPHOSATE

This invention relates to a formulation and in particular to a formulation of the herbicide glyphosate.

5 Formulations of the herbicide glyphosate are generally available in the form of a concentrate which is diluted with water by the user prior to application. For large-scale agricultural use the dilution of the concentrate normally takes place in a spray tank from which the diluted product is applied through a suitable spraying apparatus. A common problem encountered is that of excessive foaming of the concentrate. Many glyphosate
10 formulations therefore contain commercially available anti-foam agents designed to minimise this problem. Anti-foam agents are normally effective at low concentration (typically of the order of 0.5 to 10 g/l, for example about 1 g/l). This concentration is much lower than that of bioperformance enhancing adjuvants which may also be present in the formulation (typically about 100 to 150 g/l), anti-foam agents are normally assumed to have
15 little or no effect on bioperformance.

We have now found that certain polyethyleneoxide alkanols are effective as anti-foam agents and, despite being present at relatively low concentration, additionally have surprising beneficial effects on bioperformance.

According to the present invention there is provided a low-foaming herbicidal
20 composition comprising glyphosate and a poly(alkylene oxide) alkanol having the formula



wherein R₁ and R₂ are methyl or ethyl, R₃ is a straight chain alkylene group containing from 5 to 12 carbon atoms, R₄ is an alkylene group containing 2 or 3 carbon atoms and n is from 4 to 20.

25 According to a further aspect of the present invention there is provided a method of reducing the foaming of a glyphosate concentrate composition having a concentration of from 240 to 550 g/l based on glyphosate acid which comprised incorporating in the composition a poly(alkylene oxide) alkanol of formula (I).

The group (OR₄)_n is suitably a poly (ethylene oxide) group, poly (propylene oxide)
30 group or a mixed poly (ethylene oxide/propylene oxide) group. In the case of compounds

having a range of degrees of alkoxyxylation, n may be an average number. It is preferred that n is from 6 to 14, for example from 6 to 10. An especially preferred value of n is about 8.

R_1 and R_2 are preferably both methyl. R_3 preferably contains from 7 to 11 carbon atoms and an especially preferred group R_3 is $-(CH_2)_{10}-$.

A preferred poly(alkylene oxide) alkanol of formula (I) is ethoxylated, propoxylated or mixed alkoxyated/propoxylated iso-tridecyl alcohol wherein the degree of alkoxylation is from 6 to 14, for example about 8.

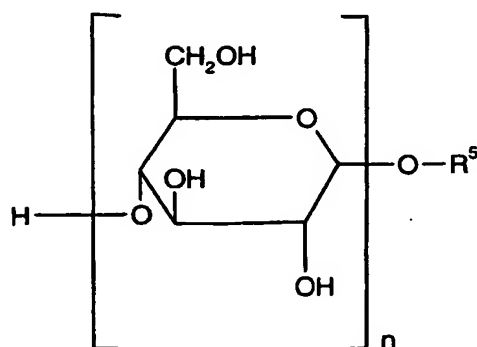
Glyphosate is normally used in the form of a water-soluble salt of glyphosate acid (N-phosphonomethylglycine) and the term glyphosate as used herein includes glyphosate acid and its salts, esters and derivatives. Typical glyphosate salts include isopropylamine, trimethylsulphonium, monoethanolamine, ammonium, potassium and sodium. As indicated previously, the present invention is particularly relevant to the formulation of glyphosate concentrates. Such concentrates typically contain of the order of 240 g/l based on glyphosate acid, although there is a move towards more concentrated formulations for example from 240 to 550 g/l, depending on the nature of the salt employed. For the potassium salt, it is possible to produce formulations having a concentration of up to 550 g/l, for example from 400 to 550 g/l and in particular around 500 g/l, whilst for the ammonium salt, more typical ranges are from 240 to 400 g/l and more particularly from 340 to 380 g/l based on glyphosate acid.

It is a particular feature of preferred aspects of the present invention that the compound of formula (I) operates both as an anti-foam and as a bioperformance enhancing agent at lower concentrations than are conventional for bioperformance enhancing adjuvants. Thus whilst higher proportions of the compound of formula (I) may be used, the benefits of the invention are most apparent when the concentration of the compound of formula (I) is below 100 g/l, for example from 0.1 to 100 g/l. A concentration of the compound of formula (I) of at least 1 g/l is preferred, for example from 1 to 50 g/l and especially from 1 to 20 g/l.

It is a further advantage of the present invention that the compound of formula (I) remains fully dispersed on storage of the composition. In contrast certain commonly used commercial anti-foams tend to separate out from the composition on storage and thereby lose their effectiveness, particularly if the concentrate is re-distributed from bulk storage into smaller containers.

It will be appreciated that relatively low levels of the compound of formula (I) are unlikely to provide sufficient bioperformance enhancement on their own and it is preferred that the compound of formula (I) is used with one or more additional bioperformance enhancing adjuvants. A wide range of bioperformance enhancing adjuvants suitable for use with glyphosate are well known in the art. We have found that the combination of a compound of formula (I) with an alkylglycoside adjuvant provides an unexpectedly high level of bioperformance enhancement of glyphosate combined with an effective anti-foam action, particularly with respect to foaming of the concentrate. The effect is of such a magnitude that it is believed that there is a beneficial interaction or synergy between the compound of formula (I) and the alkylglycoside.

The alkylglycoside for use in the present invention may be obtained by the reaction of alkanols with glucose or other mono- or di- or polysaccharides. As used herein the term "alkylglycoside" includes an alkylmonoglycoside and an alkylpolyglycoside. Preferred alkylglycosides for use in the present invention are alkylglucosides obtained by the reaction of glucose with a straight or branched chain alkanol or mixture of alkanols, for example a mixture of alkanols containing 7 to 18, preferably 7 to 16 carbon atoms for example 8 to 10 carbon atoms. The number of glucose groups per alkyl group in the molecule may vary and alkyl mono- or di- or polyglucose or saccharide derivatives are possible. Commercial alkylpolyglucosides usually contain a mixture of derivatives having an average number of glucose groups per alkyl group. Thus alkylglycosides have the general formula (III)



(III)

wherein n is the degree of polymerisation and is typically within the range from 1 to 3, for example from 1 to 2, and R^5 is a branched or straight chain alkyl group having from 4 to 18 carbon atoms or a mixture of alkyl groups having an average value within the given range. Typical of alkylglycosides is the product commercially available under the trade names AL2042 and AL2575 (Uniqema) and AGRIMUL PG2067 (Henkel Corp) wherein n is an

average of 1.7 and R⁵ is a mixture of octyl (45%) and decyl (55%), the product commercially available under the trade name AGRIMUL PG2069 (Henkel Corp) wherein n is an average of 1.6 and R⁵ is a mixture of nonyl (20%), decyl (40%) and undecyl (40%) and the product commercially available under the trade name BEROL AG6202 (Akzo Nobel) or AGRIMUL
5 PG 3399 (Henkel Corp) which is 2-ethyl-1-hexylglycoside.

The additional bioperformance enhancing adjuvant, for example the alkylglycoside, is suitably used at conventional concentrations of from about 80g/l to about 250g/l, for example from about 100g/l to about 150g/l and the ratio of the compound of formula (I) to the second bioperformance enhancing adjuvant is preferably from about
10 1 : 1 to 1 : 100 and more preferably from 1 : 10 to 1 : 40.

The compound of formula (I) may be used as the sole anti-foam agent or may be used in combination with or as a partial replacement for another anti-foam agent. The compound of formula (I) is primarily intended to reduce foaming of the concentrate. Other anti-foams whose primary purpose is to reduce foaming of the diluted product may be used in addition
15 to the compound of formula (I). A typical example of an anti-foam for reducing foaming of the diluted product is MSA supplied by Dow Corning which consists of a polydimethyl siloxane oil blended with hydrophobic silicas.

Other conventional additives such as humectants, activity enhancers (such as inorganic ammonium salts), anti-freeze agents, wetters, or other additional surfactants may
20 be added if desired. Similarly, additional water-soluble herbicides or other agrochemicals such as fungicides and insecticides may be incorporated if desired but the present invention is primarily concerned with compositions in which the only active agrochemical ingredient is glyphosate.

When diluted for use, compositions of the present invention are active against a broad
25 range of weed species including monocotyledonous and dicotyledonous species. The compositions are suitably applied directly to unwanted plants (post-emergence application).

Thus according to a further aspect of the present invention there is provided a process of severely damaging or killing unwanted plants which comprises diluting a concentrated composition of the present invention and applying to the plants a herbicidally effective
30 amount of a said diluted composition.

The rate of application of the composition of the invention will depend on a number of factors including, for example, the identity of the plants whose growth is to be inhibited and whether the compound is to be applied for foliage or root uptake. As a general guide,

however, an application rate of from 0.001 to 20 kilograms per hectare is suitable while from 0.025 to 10 kilograms per hectare may be preferred.

It is especially preferred that the glyphosate is in the form of the potassium salt or an ammonium salt. The present invention is illustrated in its application to the formulation of potassium and ammonium glyphosate respectively but is not limited to these glyphosate products. Ammonium and potassium glyphosate are particularly suitable salts for use in high-strength glyphosate concentrates in which an effective proportion of a surfactant system and inorganic adjuvant is "built-in" to the composition. The term "built-in" as used herein indicates a composition in which the required primary adjuvants are contained within a physically stable concentrate composition and do not have to be added during the tank mix stage. This does not of course preclude the operator adding further adjuvants during tank mix if desired, but there is no necessity for the addition of further adjuvants. The difficulties of providing effective high-strength glyphosate concentrates containing adjuvant systems are considerable, since such concentrates have to be physically stable over extended storage at the possible extremes of ambient temperatures likely to be encountered in commercial usage.

As used herein, the term "high-strength" aqueous glyphosate concentrate indicates a concentrate in which the glyphosate concentration is greater than 240 g/l based on glyphosate acid content, for example from 240 to 550 g/l such as from 240 to 400 g/l. An especially preferred concentration for use with ammonium glyphosate formulations is from 340 to 380 g/l based on glyphosate acid. For the potassium salt, it is possible to produce formulations having a concentration of up to 550 g/l, for example from 400 to 550 g/l and in particular around 500 g/l. It should be noted that, unless otherwise stated, all concentrations of glyphosate are given herein in terms of the percentage by weight of glyphosate acid even when the glyphosate anion is balanced by a suitable cation.

The ammonium glyphosate composition may alternatively be thought of as a combination of the ammonium salt of glyphosate, an ammonium salt such as ammonium sulphate or diammonium phosphate and the alkylglycoside. It will be appreciated however that once in solution, the composition is characterised by a total ammonium cation content balanced by glyphosate anion and, for example sulphate anion. It is convenient nevertheless to express the content of the formulation in terms of ammonium salt content and ammonium glyphosate content. The ammonium glyphosate composition of the present invention provides a physically stable composition even at a high loading of ammonium salt, for example ammonium sulphate, without having to reduce either the surfactant concentration or

the glyphosate concentration. This is particularly surprising in view of the high electrolyte content of the composition. Thus to achieve a satisfactory enhancement of the activity of glyphosate, it is desirable to incorporate more than 70 g/l ammonium salt and preferably more than about 80 g/l. The upper limit of content of ammonium salt will depend on the
5 desired content of surfactant and glyphosate ion and whilst levels as high as 180 g/l may be used if desired, the practical upper limit of the content of ammonium salt will normally be 160 g/l, or more preferably 150 g/l. Especially effective results are obtained with a content of ammonium salt of from 80 to 140 g/l since a surprisingly high and effective loading of glyphosate ion and alkylglycoside surfactant respectively may be obtained in such
10 compositions.

As noted above, whilst the ammonium ion present in the aqueous ammonium glyphosate composition should not be thought of as being associated specifically with either with the glyphosate anion or for example the sulphate anion, it is convenient to express the concentration of ammonium ion relative to glyphosate ion as being in addition to that present
15 in the "ammonium salt" such as ammonium sulphate. Thus the molar ratio of ammonium ion (in excess of that in the "ammonium salt") to glyphosate anion is preferably from 1.5 : 1 to 2 : 1, for example from 1.7 : 1 to 1.9 : 1. Particularly effective results are obtained at a ratio of (excess) ammonium ion to glyphosate ion of about 1.9 : 1.

As noted above, the content of the alkylglycoside surfactant system in the aqueous
20 concentrate is generally from about 80 to 250 g/l. The upper limit of 250 g/l is more appropriate when relatively lower levels of ammonium salt are used whilst the lower limit of 80 g/l is more appropriate when relatively higher levels of ammonium salt are used. Preferably therefore when the content of the ammonium salt content is from about 80 to about 100 g/l, the content of the alkylglycoside is from about 250 g/l to about 200 g/l, for
25 example from about 245 g/l to about 210 g/l. When the content of the ammonium salt is from about 100 g/l to about 150 g/l, the content of the alkylglycoside is from about 140 g/l to about 200 g/l, for example about 140 g/l to about 175 g/l. The potassium salt is generally less sensitive to the presence of alkylglycoside and the optimum bioperformance enhancing level may be selected for the concentration of glyphosate to be used.

30 It is a particular advantage of the ammonium and potassium glyphosate composition of the present invention that a single surfactant, the alkylglycoside may be used as the sole additional bioperformance enhancing agent with the compound of formula (I), thus providing processing and supply advantages.

If desired however, a proportion of the alkylglycoside in the glyphosate composition (whether it is ammonium or another salt) may be replaced by an alkoxyated alkylamine and in some circumstances a further increase in biological activity may be observed thereby. The phrase "alkylglycoside surfactant system" as used above includes both the alkylglycoside and the alkoxyated alkylamine, if used and the preferred concentrations given above thus include both the alkylglycoside surfactant and the alkoxyated alkylamine, if used.

The ratio of alkylglycoside to alkoxyated alkylamine in the alkylglycoside surfactant system is preferably from about 1 part by weight of alkylglycoside per 1 part by weight of alkoxyated alkylamine to about 10 parts by weight of alkylglycoside per 1 part by weight of alkoxyated alkylamine. An especially preferred ratio is from about 5 to about 8 parts by weight of alkylglycoside per 1 part by weight of alkoxyated alkylamine.

Suitably the alkyl group in the alkoxyated alkylamine contains from 8 to 22 carbon atoms (or an average of from 8 to 22 carbon atoms if a mixture of alkyl groups is present) and may be linear or branched. It is especially preferred that the alkyl group contains from 10 to 20 carbon atoms. Specific examples of preferred alkoxyated alkylamines are alkoxyated derivatives of cocamine, tallowamine, oleylamine and stearylamine. Typically such alkoxyated alkylamine surfactants are available with an average degree of alkoxylation of from 1 to about 15. Suitable alkoxy groups include ethoxy, propoxy or a mixture thereof. Ethoxy is particularly preferred.

Whilst it is possible to use an alkoxyated alkylamine in the composition of the present invention having an average degree of alkoxylation (or more specifically ethoxylation) in the commercially available range, for example from 1 to about 15, we have found that ethoxyated alkylamines having a high degree of ethoxylation are less compatible with the high-strength composition than are those having a lower degree of ethoxylation. Thus it is preferred that the average degree of alkoxylation (or more specifically ethoxylation) is from 2 to 12. Thus it is especially preferred that the average degree of alkoxylation (or more specifically ethoxylation) is from 2 to 5. An example of a particularly suitable alkoxyated alkylamine is an ethoxyated alkylamine having an average degree of ethoxylation of about 2 or about 5, for example an ethoxyated cocoamine having an average degree of ethoxylation of about 2 or about 5.

Whilst advantages may be obtained through the replacement of a proportion of the alkylglycoside with an alkoxyated alkylamine, such advantages are offset by an increase in viscosity of the composition.

If the viscosity of the composition is high, for example if an alkoxyated alkylamine is used, it may be appropriate to add a viscosity modifying agent. Suitable viscosity modifying agents include propylene glycol.

The compositions of the present invention may be made by mixing the components in the desired proportions. The particular combination of ions in the composition of the present invention may be obtained from a range of different starting materials. The order of addition is not particularly important. Thus for example solid diammonium glyphosate and glyphosate acid (to give the desired ammonium to glyphosate ion ratio) may be added with solid ammonium sulphate into water into which the alkylglycoside has been dissolved.

10 Alternatively ammonia may be added to glyphosate acid in the presence of ammonium sulphate or alternatively still, ammonia may be added to glyphosate acid in the presence of sulphuric acid.

Compositions of the present invention may also be provided in a diluted and ready-to-use form. Additional adjuvants suitable for ready-to-use formulations may also be added

15 e.g. antifreeze, polymers and dyes.

The invention is illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

In the following Examples, compositions were prepared by adding ammonia to neutralise glyphosate acid (PMG acid) in the form of an aqueous slurry in order to generate the desired ratio of ammonium ion to glyphosate (1.9 : 1). The remaining components were added in the indicated proportions (% w/w) and water was added proportionately to make up the balance. The compound of formula (I) was GENAPOL X080, iso-tridecyl alcohol having 8 polyethylene oxide units (n in formula (I) is 8). The alkylglycoside was AL2575, from UNIQEMA.

A comparison was prepared in which no compound of formula (I) was used. The quantity of alkylglycoside was increased proportionately and additional anti-foam was added.

Both the composition of the invention and the comparison with added conventional antifoam had satisfactory and essentially equivalent foaming characteristics.

In the following Table, compositions are given as % w/w at a composition density of 1.28 g/cm³:

Table 1

	Example 1	Comparison
Glyphosate acid (as technical wet paste)	28	28
Ammonia (anhydrous)	8.2	8.2
Sulphuric acid (96% Commercial)	8.5	8.5
AL2575	13.0	13.4
Antifoam MSA	0.05	0.05
Fluowet PL80	0	0.055
Isotridecyl alcohol 8EO	5.0	0
Water	To 100%	To 100%

Fluowet PL80 is 50:50 mix of perfluorinated alkyl phosphinic and perfluorinated alkyl phosphonic acid, supplied by CLARIANT. Antifoam MSA is based on polydimethylsiloxane supplied by Dow Corning.

EXAMPLE 2

The compositions of Example 1 (composition of the invention and comparison) were applied at the indicated rates expressed as glyphosate acid equivalent/ha to plant species grown in the glasshouse. All treatments were made up in tap water and applied using a track-sprayer with a 11002 nozzle at a spray application volume of 200l/ha. All treatments were replicated 3 times. After spraying the plants were laid out in a glasshouse and maintained at a temperature of 24°C by day and 19°C by night. A visual assessment of % control, where 0=unaffected and 100=complete kill, was carried out 22 days after treatment.

Table 2

% Control Against Indicated Species

Composition	Rate	AVEFA	BRODI	CHEAL	LOLRI	RAPRL
Comparison 1	240	32	3	57	7	20
	360	76	42	78	53	55
	540	86	87	92	73	85
	720	100	93	93	98	92
Example 1	240	48	15	87	25	58
	360	65	85	87	78	80
	540	62	100	92	95	73
	720	96	100	99	100	93

The species tested were: -

AVEFA Wild Oat (*Avena fatua*)

15 BRODI *Bromus diandrus*

CHEAL common lambsquarters (*Chenopodium album* L.)

LOLRI *Lolium rigidum*

RAPRL *Raphanus raphanistrum*

EXAMPLES 3 and 4

In the following Examples, compositions were prepared by adding potassium hydroxide to neutralise glyphosate acid (PMG acid). The remaining components were added in the indicated proportions (g/l) and water was added proportionately to make up the balance. The compound of formula (I) was GENAPOL X080, iso-tridecyl alcohol having 8 polyethylene oxide units (n in formula (I) is 8). The alkylglycoside was AL2575 (or the equivalent AGRIMUL PG2067) and was used in combination with an ethoxylated cocoamine having a degree of ethoxylation of 5. A comparison (Comparison 2) was

prepared in which no compound of formula (I) was used. . The foaming characteristics of the composition of the invention and comparison were measured using the standard method of CIPAC MT 47.2 are the results are shown in Table 4.

Table 3

Component	Example 3	Example 4	Comparison 2
Glyphosate acid 100%	500	500	500
Potassium hydroxide (KOH) 50%	371	371	371
AL2575	171	171	171
Alkoxylated cocoamine	46	46	46
Genapol X080	2.74	6.85	0.0
Water	To 1 litre	To 1 litre	To 1 litre

5

Table 4

	Foam height at 10 seconds (mm)	Foam height at 60 seconds (mm)	Foam height at 180 seconds (mm)	Foam height at 720 seconds (mm)
Comparison 2	45	60	50	44
Example 3	8	18	16	6
Example 4	14	18	20	18

EXAMPLES 5 and 6

In the following Examples, compositions were prepared by adding potassium hydroxide to neutralise glyphosate acid (PMG acid). The remaining components were added in the indicated proportions (g/l) and water was added proportionately to make up the balance. The compound of formula (I) was GENAPOL X080, iso-tridecyl alcohol having 8 polyethylene oxide units (n in formula (I) is 8). The alkylglycoside was AGRIMUL PG 3399 and was used in combination with an ethoxylated cocamine having a degree of ethoxylation of 5. AGRIMUL PG 3399 is a low-foaming alkylglycoside. A comparison (Comparison 3) was prepared in which no compound of formula (I) was used.

The foaming characteristics of the composition of the invention and comparison were measured using the standard method of CIPAC MT 47.2 are the results are shown in Table 6.

Table 4

Component	Example 5	Example 6	Comparison 3
Glyphosate acid 100%	500	500	500
Potassium hydroxide (KOH) 50%	371	371	371
AGRIMUL PG 3399	184	184	184
Alkoxylated cocoamine	46	46	46
Genapol X080	2.74	6.85	0.0
Water	To 1 litre	To 1 litre	To 1 litre

Table 5

	Foam height at 10 seconds (mm)	Foam height at 60 seconds (mm)	Foam height at 180 seconds (mm)	Foam height at 720 seconds (mm)
Comparison 3	38	36	32	20
Example 5	10	18	16	10
Example 6	18	24	24	24